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TECHNICAL REPORT

Investigation of Novel Glass Scintillators for Gamma Ray Detection

February 2013

HDTRA1-07-1-0017

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14. ABSTRACT
Develop a new class of high performance, large volume, low cost gamma-ray detectors. A unique approach to combine the high sensitivity of inorganic crystal scintillators with chalcogenide glass and glass ceramic technology. The material development effort will be aided by a new capability in time-resolved ultrafast X-Ray spectroscopy.

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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY →	BY →	TO GET
TO GET ←	BY ←	DIVIDE
angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter^2 (m^2)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm^2)	4.184 000 x E -2	mega joule/m^2 (MJ/m^2)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^\circ f + 459.67)/1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter^3 (m^3)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch^2 (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m^2 ($N-s/m^2$)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot^2	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch^2 (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot^2 (moment of inertia)	4.214 011 x E -2	kilogram-meter^2 ($kg-m^2$)
pound-mass/foot^3	1.601 846 x E +1	kilogram-meter^3 (kg/m^3)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0^0 C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

Objectives: Develop a new class of high performance, large volume, low cost gamma-ray detectors. Our unique approach is to combine the high sensitivity of inorganic crystal scintillators with chalcogenide glass and glass ceramic technology. The material development effort will be aided by a new capability in time-resolved ultrafast X-ray spectroscopy (See Fig. A). We will probe the dynamics of charge transport in the first picoseconds after an ionizing event. This will provide new insight on both deleterious trapping and chromophore capture that can be used to engineer and optimize scintillators.

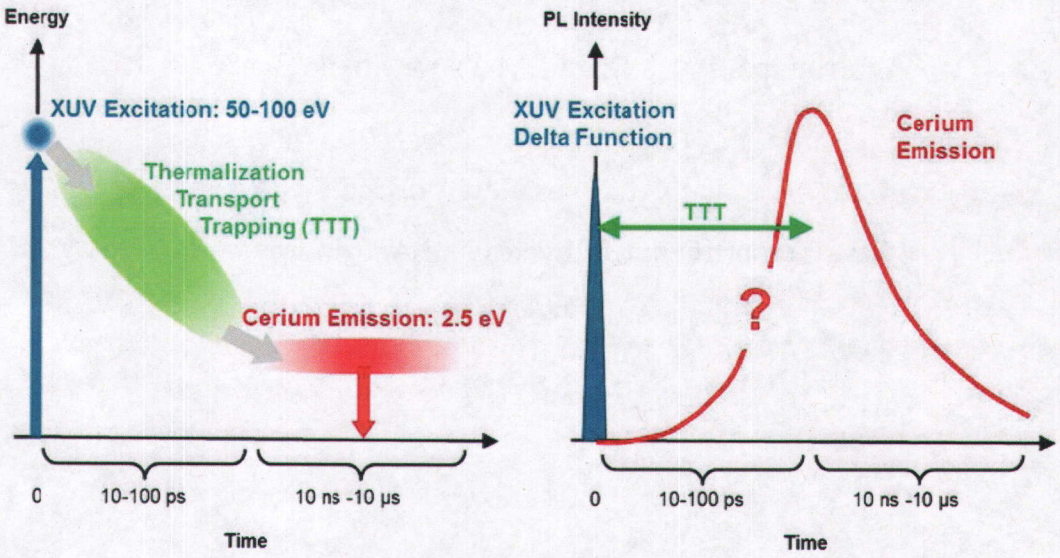

Fig. A Investigation of ultrafast scintillation dynamics involving thermalization, transport and trapping using XUV bursts.

Accomplishments:

Material Synthesis Effort:

The scintillator fabrication efforts at LANL made significant progress during this period. We have seen an optimization of both photo-luminescence and scintillation properties of cerium-doped gallium-sodium-sulfide (GNS:Ce^{3+}) glass. The observation of scintillation is an important milestone that had eluded us in our initial work. Of note is what we believe to be the first observation of X-ray excited emission in a sulfide glass. This was achieved by optimizing the material bandgap with a CsCl glass modifier.

The baseline matrix is Ga_2S_3-Na_2S (GNS) glass doped with 1% $CeCl_3$ and different amounts of CsCl. The CsCl serves as a glass modifier that blue-shifts the bandgap (see Fig.1). CsCl is ionic and penetrates the covalent gallium-sulfide glass network. This decreases the average covalency and increases the band-edge energy, enhancing the Ce^{3+} quantum yield (see Fig. 2).

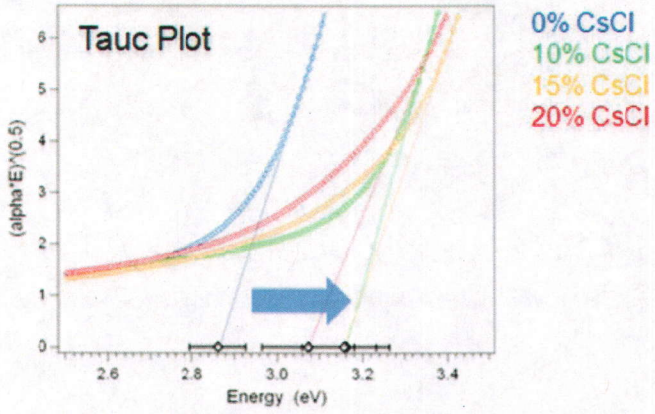

Fig.1 : *Addition of CsCl to GNS glass blue-shifts the band edge by ~0.25 eV and enhances the Ce^{3+} photoluminescence quantum yield.*

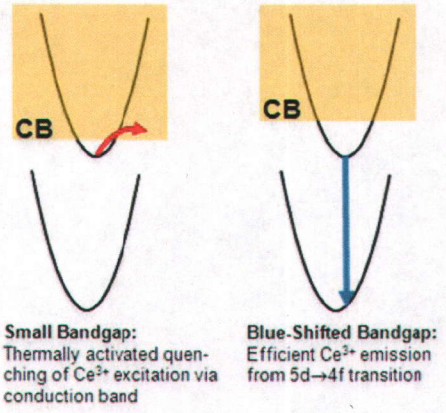

Fig. 2: *Effect of conduction band edge position on the relaxation dynamics of the Ce^{3+} excited state.*

The key here was refining the synthesis procedure to compensate for evaporative loss of CsCl during glass melting CsCl has the highest vapor pressure of the glass constituents and partially evaporates. To combat this problem, the melt was biased with excess CsCl to exactly compensate the evaporative loss. Optimized GNS:Ce,Cs glass showed efficient photoluminescence in the green when excited with a cw light-emitting diode at 435 nm at 300 K (see photograph in Fig.3). Figure 3 depicts the scintillation spectrum from such a GNS glass doped with 20% CsCl and 1% Ce^{3+} X-ray excited with 25 keV X-rays at 300 K.

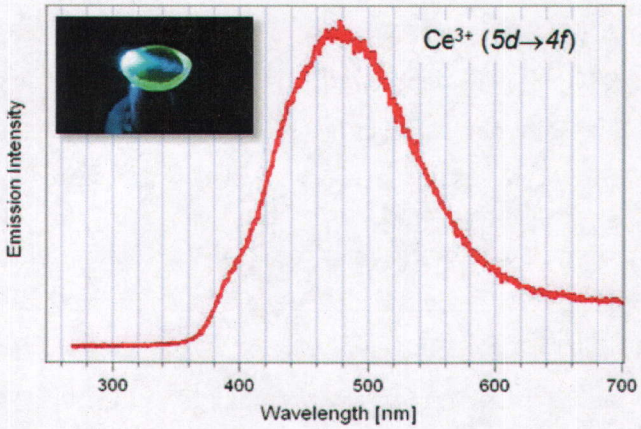

Fig. 3: *X-ray excited (25 keV) emission spectrum at 300 K in GNS glass doped with 20% CsCl and 1% Ce^{3+}. The insert shows the green photoemission of this sample obtained under cw excitation by a blue (435 nm) light-emitting diode.*

Characterization Effort:

With the hiring of a postdoctoral researcher (Dr. Mahenrda Shakya) from Kansas State University, we began construction of the ultrafast XUV characterization system in Oct. 2007. Using supplemental funds from a DTRA congressional funding, we acquired a 1 kHz, 3.5 millijoule (3.5 W) amplifier system (Coherent Legend II).

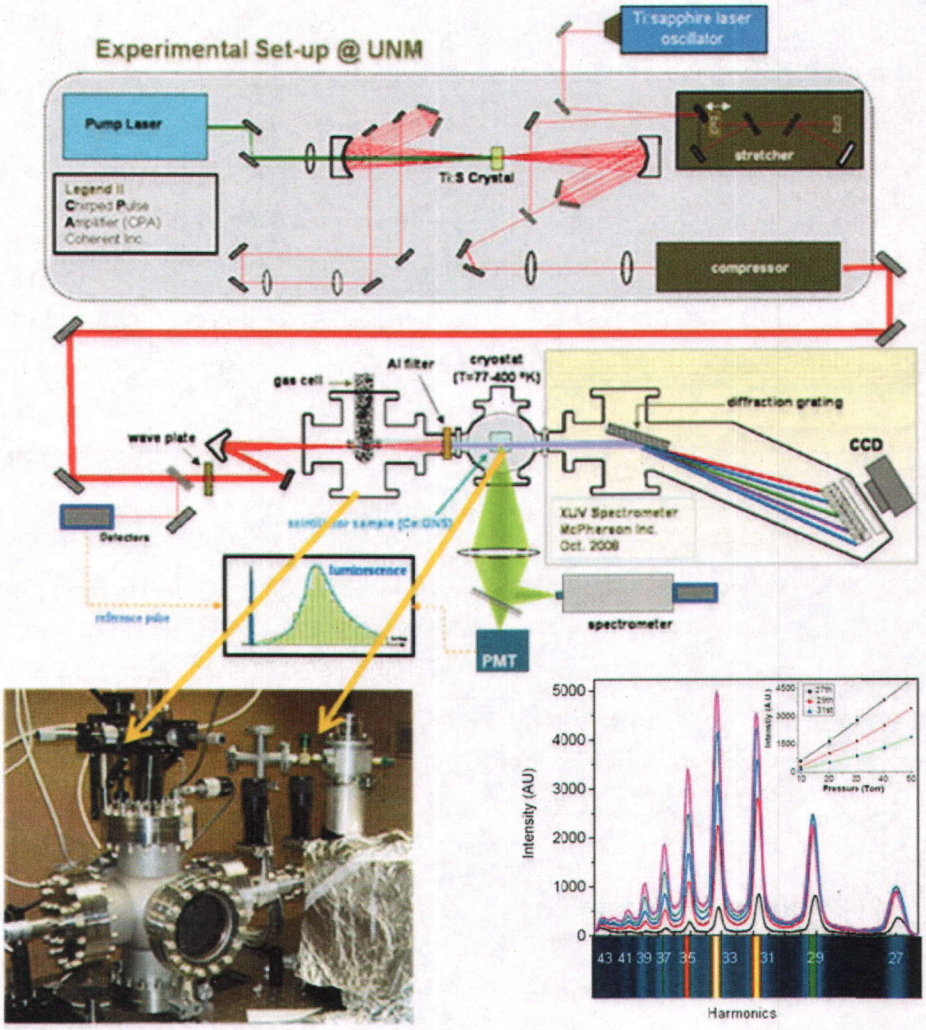

Fig. 4 ***Top****: The ultrashort (<30 fs) XUV pulse generation system at UNM. A Ti:sapphire oscillator (λ=800 nm) seeds a regenerative chirped pulse amplifier (CPA) operating at 1 kHz, producing >3.5 mJ pulses having 35 fs duration. These pulses are then focused into a 50-100 torr Ar gas cell generating >50 eV XUV pulses. After filtration, the XUV pulses are incident on the scintillator target situated in a LN2 cryostat. The time-resolved luminescence is collected with a fast PMT.* ***Bottom:*** *(left) Photo of the XUV cell and the cryostat in our laboratory.(right) The spectrum of a typical XUV pulse generated using HHG process in Ar gas. The highest efficiency is shown to be at the 33rd harmonic (λ≈24 nm) corresponding to a photon energy of ~ 51 eV.*

As shown in Fig. 4, the major portion of the ultrafast XUV system for dynamic transport characterization of the

scintillators is now in place. Amplified laser pulses having 35 femtosecond duration and >3 mJ energy are focused into a carefully designed chamber containing noble gases of Ar, Ne or Helium. The intense electric field ionizes these atoms, accelerates the ionized electron and, within one optical cycle, smashes the electon into the parent ion thus producing an XUV bursts. This process is called high-harmonic-generation (HHG) and has been also employed to generate attosecond pulses in a number of groundbreaking experiments in recent years. We are the first to exploit this short bursts of XUV radiation to investigate transport dynamics of scintillators in order to understand the electron- chromophore capture rates and subsequent quantum yield correlations at various temperatures. To achieve this, the XUV pulse is exited through an aluminum filter (to remove the IR laser background), entering a liquid nitrogen (LN2) cryostat which houses the scintillator material at a controllable temperature of 70-400 K. The initial experiments were conducted on a commercially available and well-known scintillator crystal (Tl:CsI) which will be used as a reference material. The resulting luminescence is then collected by a high numerical aperture lens and is detected by a high speed photomultiplier tube (PMT).

For calibration purposes, we investigated time-resolved scintillation in a standard Tl:CsI which is known to have a Light Output (LO) > 65,000 photons/MeV. We measured rise-time and decay-time of the luminescence as a function of temperature from T=300 to 100 K as shown in Fig. 5. Our preliminary experiments on GNS glasses exhibit much faster dynamics (rise-time) than CsI as shown in Fig. 5.

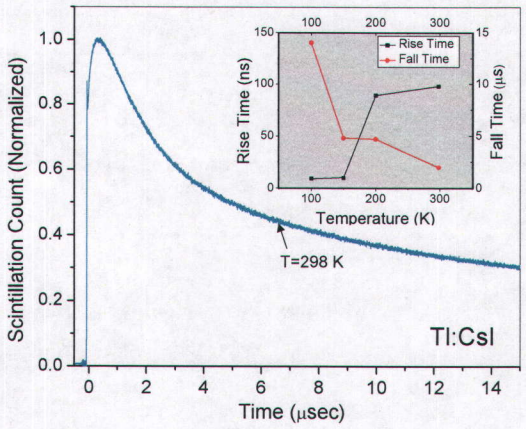

Fig. 5 *Time-resolved scintillation count due to femtosecond XUV (≈50 eV) excitation in Tl:CsI at room temperature. The inset shows the measured rise-times and fall-times versus temperature. These data are consistent with that of Ref. [1, 2]*

We completed the construction of the ultrafast XUV characterization system. Using supplemental funds from a DTRA congressional funding and an NSF MRI grant, we acquired an amplifier (Coherent Legend II) and an XUV spectrometer (Model 248/310G-1, McPherson Inc.) that are now integrated with the XUV system as shown in Figure 4.

We are the first to use these short bursts of XUV radiation to probe transport dynamics of scintillators. We wish to understand the electron-chromophore capture rates and subsequent quantum yield correlations at various temperatures. To achieve this, the XUV pulse exits the generation cell through an aluminum filter that removes the IR laser background. It then enters a liquid nitrogen (LN2) cryostat that houses the scintillator material at an adjustable temperature of 70-400 K.

Initial experiments are conducted on a commercially available and well-characterized scintillator crystal (Tl:CsI) that serves as a reference material. Tl:CsI is known to have a Light Output (LO) > 65,000 photons/MeV and exhibits a long risetime (>10 ns), which makes scintillation dynamics accessible with standard detectors and electronics.

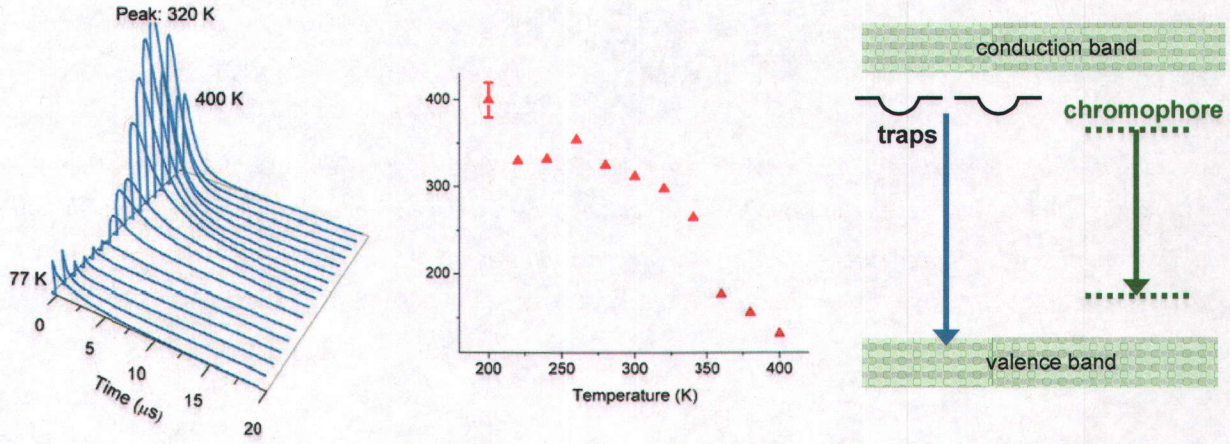

Fig. 6 *(left) The time-resolved scintillation traces of Tl:CsI after excitation with short bursts (~ 20 fs) of XUV (spectrum shown in Fig. 4) at various temperatures. (center) The observed temporal behavior and temperature dependence of the rise time (right panel) is indicative of a shallow trap model. (right) An energy diagram describing the role of traps in a scintillator material. Carriers can be captured by traps thus inhibiting the transport to the chromophore. The capture duration decreases as temperature is raised due to thermal ionization. This temperature behavior is opposite for the chromophores as their luminescence gets quenched at higher temperatures.*

In the first set of experiments, scintillation time traces are measured as a function of temperature ranging from 400K to 77K, as shown in Fig. 6.

After establishing a baseline performance with Tl:CsI, we turn our attention to investigating Ce:GNS glass scintillators synthesized by our collaborators at LANL. The scintillation traces after ultrashort XUV excitation are shown in Fig. 7 for various temperatures. We note that, unlike Tl:CsI, the quantum yield (i.e. the scintillation signal) of the Ce:GNS sample increases as temperature is lowered to 77K.

The thermal quenching process is as a consequence of proximity of the Ce^{3+} 5d level to the conduction bad of GNS. This separation can be controlled by addition of CsCl modifier. More discussion of this is presented later.

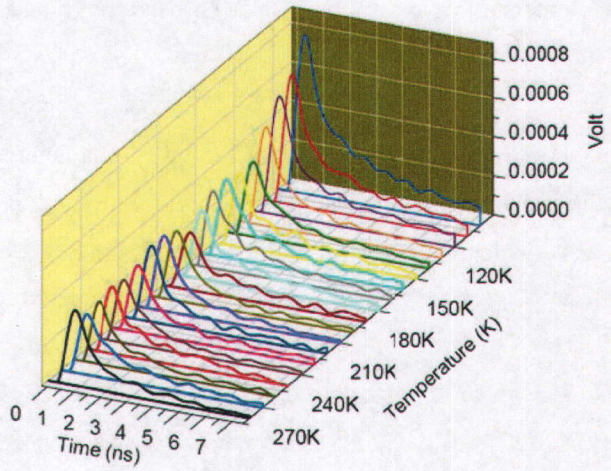

Fig. 7 *Time-resolved scintillation traces of Ce:GNS after excitation with short bursts (20 fs) of XUV (spectrum shown in Fig. 4) at various temperatures. The observed temperature dependence shows that the scintillation yield is dominated by luminescence quenching of the chromophore*

Ultrafast Rise-time Characterization Using Picosecond Kerr Gating:

The transport dynamics (i.e. rise and decay time characteristics) of the Tl:CsI are long enough that conventional detectors and electronics can resolve them. This is not typical of most scintillators, where rise times are most often on the 1-100 ps time scale. To resolve such fast transients, we are using a Kerr-gating technique as shown in Fig. 8.

This configuration has now been set up in our laboratory. For calibration purposes we measured the gating of the second harmonic pulse (at λ=400 nm). The result is shown in the inset of Fig. 8, indicating a response time of about 5 ps. Work is underway to apply this unique capability to investigate the risetime of various inorganic scintillators including the novel materials synthesized by our LANL collaborators.

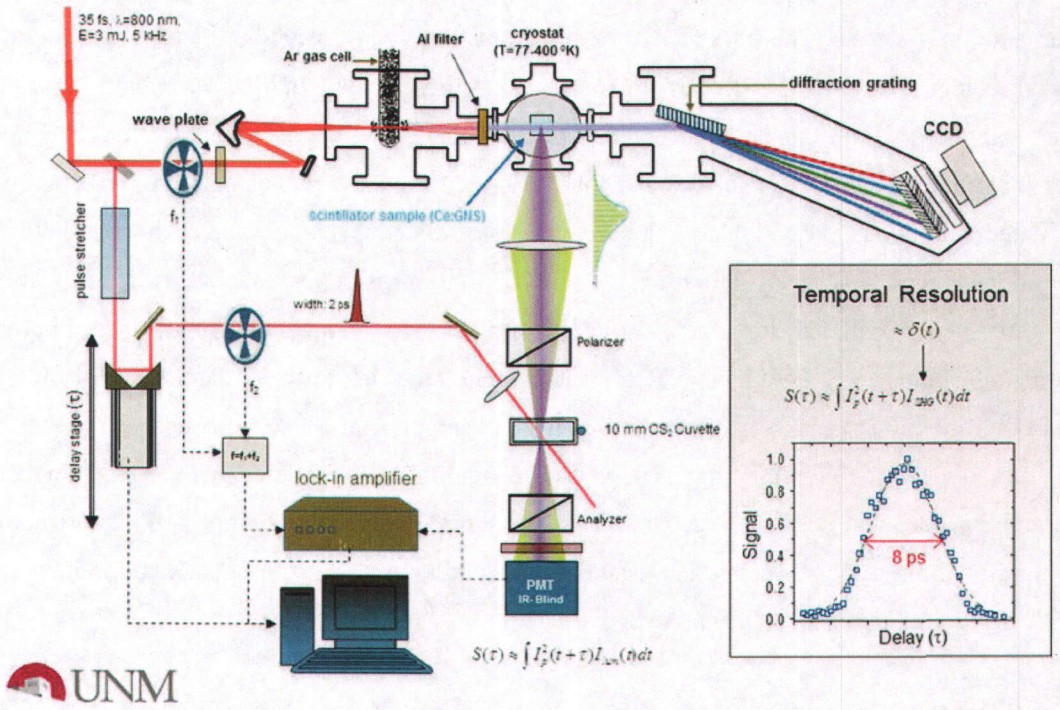

Fig. 8. *Ultrafast time-resoled luminescence dynamics measured using Kerr-gating technique. A time delayed gate pulse induces a birefringence in the Kerr media that rotates the polarization to momentarily transmit luminescence. The inset shows the measured Kerr gating of the second harmonic (SHG) of the IR pump pulse using a 10 mm CS_2 cell indicating a response time of about 5 ps.*

Kerr-gating Investigation of GNS using 2nd and 3rd harmonics:

Using 2nd (λ~400 nm), and 3rd (λ~267 nm) of the Ti:sapphire pulses the scintillation (luminescence) dynamics were measured at room temperature. The data is shown in Fig. 9. It indicates that at 400 nm, the chromophores are directly excited and thus the ensuing luminescence does not involve any transport leading to a fast (18 ps) rise time. The exciation in UV (at 267 nm), however, involves absorption in the host material with subsequent transfer to the chromophores at a much longer delay time (>400 ps).

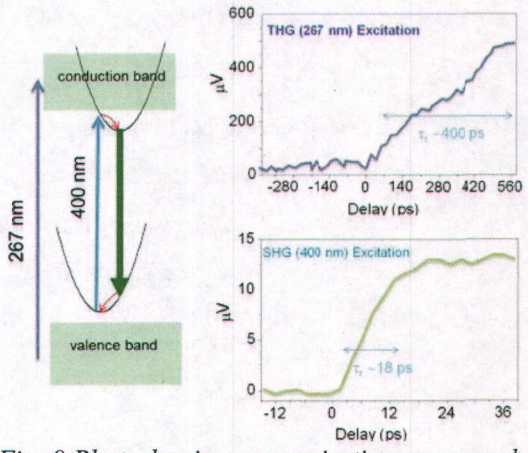

Fig. 9 Photo-luminescence risetime measured using ultrafast Kerr-gating when excited with ultrashort pulses at 400nm and 267 nm.

Growth of Nano-Structured Glass-Ceramic Scintillators:

With rather poor performance of the Ce:GNS scintillators, our focus was shifted towards Ce-doped glass ceramics scintillators. Several approaches are currently being pursued in the community to create high-performance scintillators that can be produced in large volumes at low cost. This includes nano-composite scintillators consisting of nano-phosphor dispersed in a polymer matrix, ceramics made from thermally sintered polycrystals, and amorphous glasses . This is a nascent field of material science, and each of these technologies faces specific technical risks and limitations. The proposed glass-ceramic scintillators are an attractive alternative to the above approaches as they can avoid many of the technical challenges these approaches are facing. Our team members at LANL have recently demonstrated the first efficient gamma-ray scintillation from a YAG:Ce glass-ceramic (see Fig.10). While this was a small sample that was opaque because of the crystallites in the glass matrix being micron rather than nano-sized, this preliminary result demonstrates the unique potential of glass-ceramics as efficient and robust gamma-ray scintillators. The proposed work will explore and optimize glass-ceramic growth processes in detail and establish the conditions that are necessary to produce transparent samples with high scintillation efficiency at low cost.

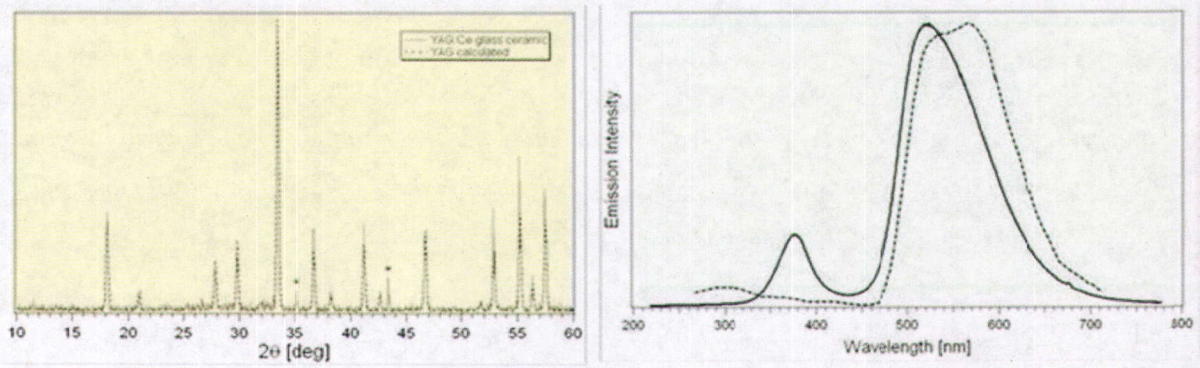

Fig. 10. (right) Radio-luminescence spectrum of YAG:Ce glass ceramic excited at 25 keV at 300 K (solid line). The YAG:Ce glass-ceramic emission is well matched with the photosensitivity of commercial silicon avalanche photodiodes (dotted line), enabling sensitive, miniature, low-cost radiation sensors. (left) X-ray diffraction data of YAGCe glass ceramics compared with that calculated for YAG single crystal, indicating the high crystalline nature of the glass ceramic islands.

Time-resolved and temperature studies on the Ce:YAG glass ceramics

The ultrashort pulse laser facility was used to investigate the transport dynamics and luminescence lifetime of newly synthesized Cerium doped YAG glass ceramics (GC) developed by our collaborators at the Los Alamos National Laboratory.

Initial experiments involved excitation of Ce:YAG-GC by femtosecond pulses at the wavelengths of 400nm and 267nm corresponding to the 2nd and 3rd harmonics of the Ti:sapphire laser system. Fig. 11 shows the 5d→4f luminescence trace of Ce^{3+} subject to 30 fs pulses at 267 nm. It is evident that two excitation mechanism exists involving electron-hope capture by Ce^{3+} (fast risetime) followed by exciton→Ce^{3+} transfer in later times.

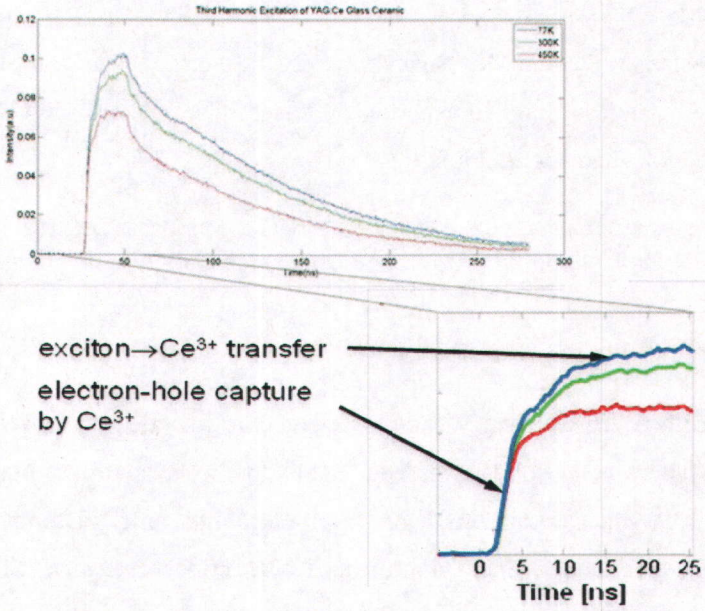

Fig. 11 Time-resolved scintillation traces in Ce:YAG glass ceramics excited by femtosecond UV laser pulses.

With the initial success of our synthesis procedure, our efforts are currently concentrated on the growth and characterization of Ce:YAG glass ceramics.

Overall Accomplishments/New Findings: Ultrafast XUV spectroscopy system based on high harmonic generation (HHG) was set up to investigate the transport dynamics of scintillator materials. This is a unique system equipped with state of the art XUV spectrometer and low temperature capability. An ultrafast Kerr gating system was constructed that will render a temporal resolution of a few picoseconds.

On the material front, Ce:GNS glasses were synthesized and their x-ray scintillation properties were demonstrated for the first time. Upon ultrafast dynamics and photon yield measurements, it was concluded that

a better approach is to investigate Ce-doped YAG glass ceramics. Subsequently, Cerium-doped YAG glass ceramics have been initially synthesized and X-ray scintillation was successfully observed. Ultrafast UV induced scintillation has been used for the first time to characterize the transport dynamics in such materials.

Personnel Supported: The grant has provided partial support for a postdoc, two graduate students (Wendy Patterson and Aram Gragossian) and one month summer salary for the PI each year.

Publications and Presentations:

- M.P. Hehlen, B.L. Bennett, A. Castro, D.J. Williams, S.C. Tornga, R.E. Muenchausen, "Synthesis and optical properties of Ga_2S_3-Na_2S-CsCl glasses", Optical Mater., 32 (2010) 491.
- Aram Gragossian, Mahendra Man Shakya, Denis V. Seletskiy, Mansoor Sheik-Bahae "Investigation of Scintillation Dynamics Using Ultrashort XUV Laser Pulses", SouthWest Optics Conference (SWOC), Albuquerque NM, June 15-17, 2009

Interactions/Transitions: Collaboration with the Los Alamos National Laboratory.

New Discoveries: Observation of X-ray scintillation in Ce:GaNaS glass and Ce:YAG glass ceramics.

Honors/Awards: The graduate student, Wendy Patterson, was awarded the LANL 2008 Student Distinguished Performance Award. This recognition is awarded annually to only a handful of outstanding students. Wendy was recognized for her successful work at LANL on developing high-purity materials for our group's laser cooling and glass scintillator project under supervision of our LANL collaborators Dr. Markus Hehlen and Dr. Richard Epstein.

*Wendy Patterson receiving the **2008 Distinguished Performance Award** from Dr. Duncan McBranch, the deputy principal associate director for Science, Technology and. Engineering (PADSTE) at Los Alamos National Laboratory on Aug. 6, 2008*

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